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# Effect of Organic and Inorganic Passivation in Quantum Dot Sensitized Solar Cells

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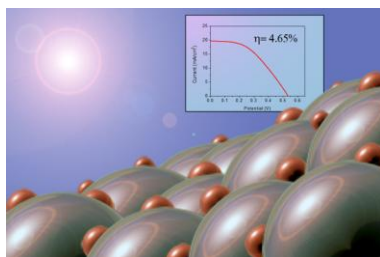
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## Abstract:

The effect of semiconductor passivation on Quantum Dot Sensitized Solar Cells (QDSCs) has been systematically characterized for CdS and CdS/ZnS. We have found that passivation strongly depends on passivating agent, obtaining an enhancement of solar cell efficiency for compounds containing amine and thiol groups while, in contrast, a decrease in performance for passivating agents with acid groups. Passivation can induce a change in the position of TiO<sub>2</sub> conduction band, and also in the recombination rate and nature, reflected in a change in the  $\beta$  parameter. Especially interesting is the finding that  $\beta$ , and consequently the Fill Factor, FF, can be increased with passivation. Applying this strategy record cells of 4.65% efficiency for PbS based QDSCs have been produced.

## TOC Figure



Keywords: Quantum Dots, Sensitized Solar Cells, Passivation

In the last few years the interest in the use of light absorbing inorganic semiconductor materials for nanostructured photovoltaic devices has increased enormously. In particular in the case of semiconductor quantum dots (QDs), when semiconductors particle size is smaller than its Bohr radius and quantum confinement regime is attained.<sup>1-7</sup> These materials are extremely interesting for the development of photovoltaic applications for several reasons: tunable band gap, high extinction coefficient, large intrinsic dipole moment, easy and cheap production.<sup>1-7</sup> In fact, QD solar cells are announced as the next big thing in photovoltaics due to the huge potentiality of these materials in several different configurations.<sup>8</sup> Among these configurations quantum dot sensitized solar cells (QDSCs), where QDs acts as light harvesters, have awakened a special interest. QDSCs benefit from the huge knowledge already achieved with dye sensitized solar cells (DSCs) and to the easy preparation of this type of devices.

In spite of its potentiality, the efficiency obtained for QDSCs has been significantly inferior than the record efficiency reported for DSCs ( $\sim 12\%$ ).<sup>9</sup> Currently, the maximum efficiency reported for CdS/CdSe light absorbing material, the most

extended semiconductors analyzed in QDSCs is  $\sim 5.4\%$ ,<sup>10, 11</sup> and up to 6.3% has been obtained with  $\text{Sb}_2\text{S}_3$ .<sup>12</sup> Very recently we have reported an efficiency for PbS/CdS QDSCs of 4.2 % (unpublished results). Nevertheless, recent reports of solar cell efficiencies exceeding 10% for all solid nanostructured devices using lead halide perovskite have boosted the interests in semiconductor nanostructured light harvesters.<sup>13, 14</sup> The exact working principles of these perovskite solar cells are not as well understood and some differences with conventional sensitized solar cells have been manifested in these devices.<sup>13</sup> Moreover these working principles have been studied for conventional QDSCs.<sup>1, 15, 16</sup> In the present work we have used this last configuration, QDSCs to study the effect of QD passivation in the final cell performance.

Passivation of QDs has helped to increase significantly the efficiency of a third kind of solar cells using, in this case, a thin layer of colloidal QDs. In this last configuration QD colloidal layer is responsible for both light harvesting and charge transport. Organic<sup>17-19</sup> and inorganic<sup>19, 20</sup> passivation have improved the solar cell performance of thin layer of colloidal QDs solar cells, attaining efficiencies as high as 7% when hybrid passivation (organic and inorganic) is used.<sup>19</sup> In the case of QDSC configuration it is well-known that the performance is improved significantly when the surface of QDs is coated with ZnS inorganic passivating agent.<sup>21-23</sup> On the other hand, several works in the literature report the functionalization of nanocrystals and metallic clusters by using a series of different organic species, including thiols,<sup>17, 18, 24, 25</sup> amines,<sup>26</sup> and carboxylic acids.<sup>27</sup> These molecules can passivate the surface states of QDs,<sup>19</sup> introduce electrical dipoles,<sup>24</sup> act as electron traps<sup>20</sup> or hole traps.<sup>25</sup>

Our work, here reported, is focussed on the effect in the performance of QDSC subjected to organic and inorganic passivation. For that purpose, we have analyzed CdS, CdS/ZnS, and PbS/CdS/ZnS QDSCs, choosing dimethylamine (DMA),

ethylenediamine (ETDA), ethanedithiol (EDT), thioglycolic acid (TGA), and formic acid (FA), as organic passivating agents, and the halides in hexadecyl trimethylammonium chloride (HTAC) and tetrabutylammonium iodide (TBAI) as the inorganic passivating ligands (Figure 1). We have observed that in many cases passivation produces a beneficial effect in cell performance, especially due to an improvement in Fill Factor, FF. We found that the increase of FF is produced by an increase of  $\beta$ , an empirical parameter related with the electron recombination rate,  $U_n$ . In sensitized solar cells.  $\beta$  is the exponent of the electron density,  $n$ :<sup>28</sup>

$$U_n = k_r n^\beta \quad (1)$$

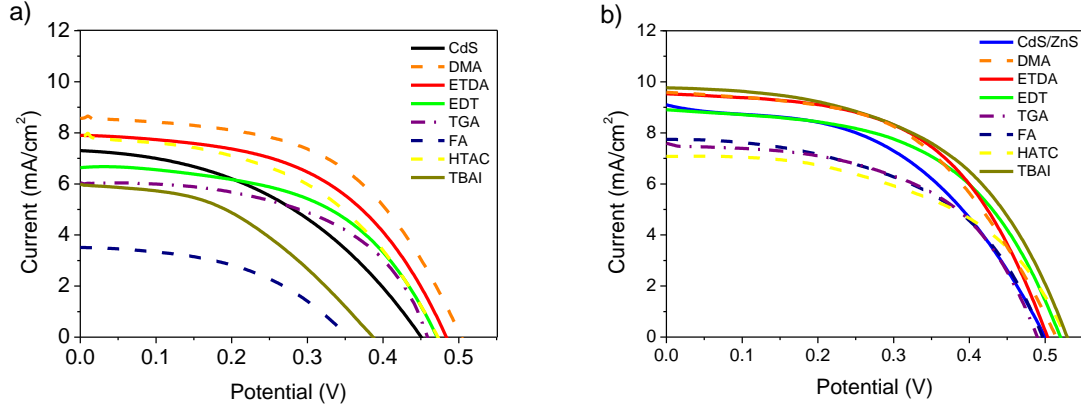
where  $k_r$  is a constant. We have used this passivation strategy to push the efficiency of PbS/CdS QDSCs up to a value as high as 4.65%, as far as we know the highest efficiency for this material and configuration.

**Figure 1:** Chemical structure of the surface passivation agents employed.

To analyze the fundamental effect of organic and inorganic passivation CdS sensitized electrodes were prepared. For comparison, the same passivation performed on CdS sensitized electrodes was also performed on CdS/ZnS sensitized electrodes. It is already known that ZnS coating enhances significantly efficiency of QDSCs due to an efficient passivation.<sup>21-23</sup> The objective of passivate CdS/ZnS sensitized electrodes was

to verify if the good passivation performed by ZnS coating could be improved. Sample preparation and characterization methods are described in detail in Supporting Information SI1. Briefly, nanostructured TiO<sub>2</sub> electrodes were sensitized by successive ionic layer adsorption and reaction (SILAR) method, and subsequently treated with the different organic ligands and inorganic precursors mentioned above. These molecules attach preferentially on the deposited semiconductor, instead of TiO<sub>2</sub>, as SILAR deposition method practically cover all the TiO<sub>2</sub> surface.<sup>15</sup> Then, these electrodes were assembled with copper sulfide counter electrodes and aqueous polysulfide electrolyte in order to prepare the corresponding devices and study their performance. At least 2 electrodes were prepared under the same conditions of sensitizer and passivation agent, but more than two cells have been prepared in the case of reference cells and cells with the highest efficiencies.

The average current-potential (J-V) characteristics of these solar cells under simulated solar illumination (AM1.5, 100 mW·cm<sup>-2</sup>) are shown in Figure 2. The solar cell parameters corresponding to these J-V curves are summarized in Table 1. Results reported in Figure 2 and Table 1 are the average values obtained in cells prepared under the same conditions. Cells based on CdS and CdS/ZnS samples without any additional passivation treatment were taken as standard reference devices. Table 1 indicates that ZnS passivation increases significantly the overall efficiency of CdS QDSCs from 1.45 to 2.23 %, as it has been previously observed.<sup>21-23</sup>



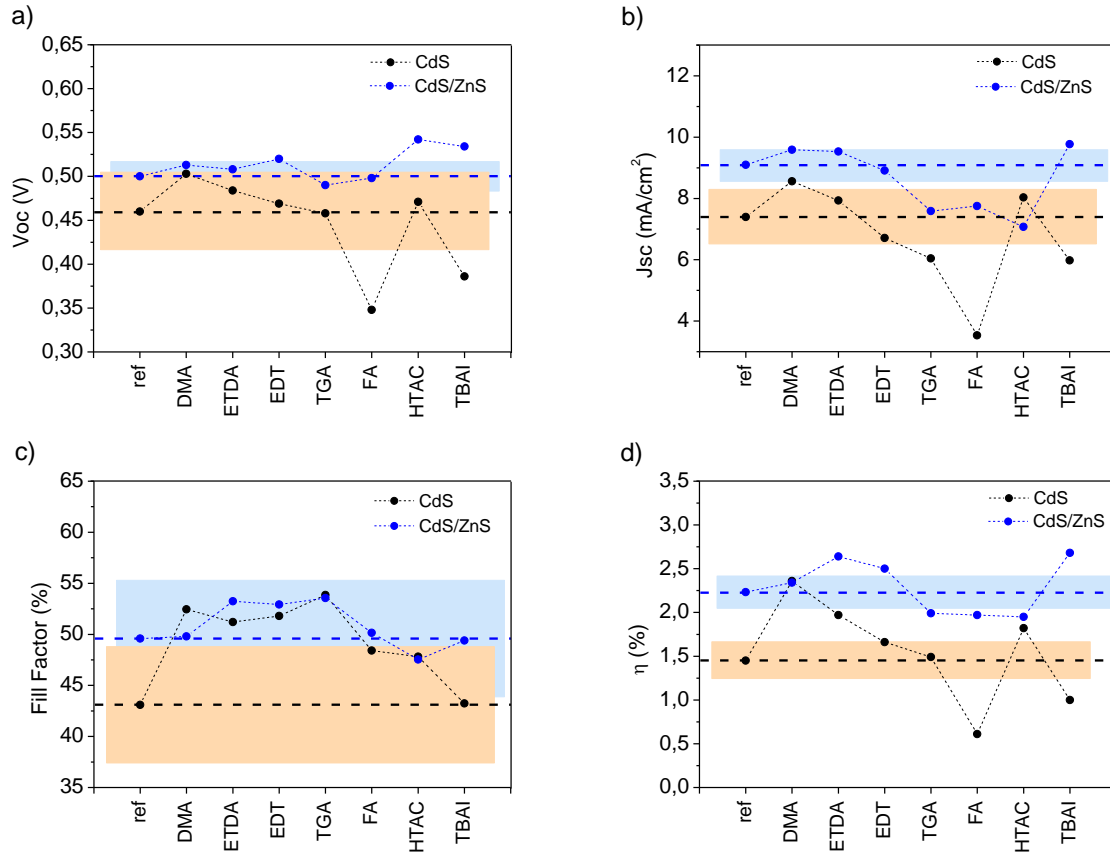
**Figure 2:** J-V curves of the (a) CdS and (b) CdS/ZnS QDSCs treated with different organic and inorganic surface passivation agents, obtained from averaging the J-V curves of cells prepared with the same conditions.

Comparing CdS and CdS/ZnS electrodes, Figures 2a and 2b respectively, broader dispersion of J-V curves with the different treatments is observed for CdS samples. Despite this dispersion some general trends can be unveiled with the help of Figure 3: i) ZnS coating enhances the short circuit current,  $J_{sc}$ , open circuit potential,  $V_{oc}$ , FF, and consequently the conversion efficiency,  $\eta$ , see dashed lines in Figure 3; ii) the effect of the other passivating agents is less significant than the effect of ZnS but the appropriated ones can enhance cell efficiency even for cells already passivated with ZnS; iii) alkylamines (DMA and ETDA) and alkylthiols (EDT) promote a clear increase on cell efficiency in comparison to the reference devices, whereas the additives bearing carboxylic groups (TGA and FA) reduces cell performance for both CdS and CdS/ZnS electrodes; iv) for inorganic passivation, the results depend on the semiconductor surface, CdS efficiency increases with  $\text{Cl}^-$  and decreases with  $\text{I}^-$ , while CdS/ZnS shows the opposite behavior; and v) especially significant is the increase of FF that cannot be explained merely by the increase of  $V_{oc}$  observed in certain samples.<sup>29</sup>

**Table 1:** Averaged cell parameters for CdS and CdS/ZnS QD-sensitized cells, plotted in Figure 2.

	<b>Voc (V)</b>	<b>Jsc (mA/cm<sup>2</sup>)</b>	<b>FF (%)</b>	<b>η (%)</b>
<b>CdS</b>	0.460	7.39	43.1	1.45
<b>DMA</b>	0.503	8.56	52.5	2.36
<b>ETDA</b>	0.484	7.93	51.2	1.97
<b>EDT</b>	0.469	6.71	51.8	1.66
<b>TGA</b>	0.458	6.04	53.9	1.49
<b>FA</b>	0.348	3.53	48.4	0.61
<b>HTAC</b>	0.471	8.03	47.8	1.82
<b>TBAI</b>	0.386	5.98	43.2	1.00
<b>CdS/ZnS</b>	0.500	9.10	49.6	2.23
<b>DMA</b>	0.513	9.59	49.8	2.34
<b>ETDA</b>	0.508	9.53	53.2	2.64
<b>EDT</b>	0.520	8.91	52.9	2.50
<b>TGA</b>	0.490	7.59	53.6	1.99
<b>FA</b>	0.498	7.75	50.2	1.97
<b>HTAC</b>	0.542	7.07	47.5	1.95
<b>TBAI</b>	0.534	9.77	49.9	2.68





**Figure 3:** Cell parameter analysis of the CdS and CdS/ZnS QDSCs treated with different surface passivation agents. The shaded areas show the standard deviation ( $\sigma$ ) for each cell parameter of the reference CdS, pink, and CdS/ZnS, blue, QDSCs, while black and blue dashed lines indicate the average value obtained for reference samples. Dotted lines are only eye guides and they cannot be considered as trend lines.

In view of the results obtained, we have analyzed our devices by impedance spectroscopy (IS) in order to find out a feasible explanation for the trends observed in the solar cell parameters after organic and inorganic passivation. Figure 4 shows the recombination resistance,  $R_{rec}$ , and chemical capacitance,  $C_{\mu}$ , extracted from the IS measurements in dark conditions. For samples sensitized with CdS, these parameters are shown in Figures 4a and 4b, whereas for CdS/ZnS,  $R_{rec}$  and  $C_{\mu}$ , are shown in Figures 4c and 4d, respectively. Both  $R_{rec}$  and  $C_{\mu}$  are represented as a function of  $V_F = V_{app} - V_{series}$ , which is the applied voltage,  $V_{app}$ , corrected by the voltage drop due to series resistance

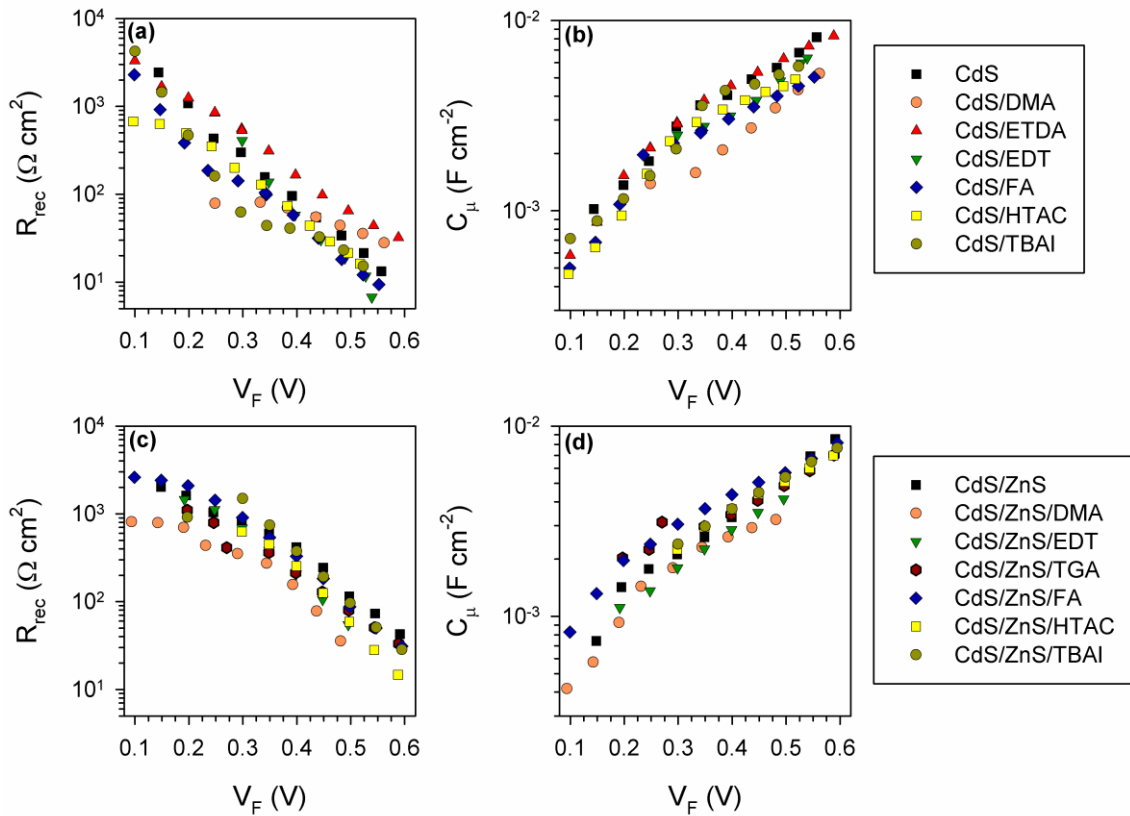
$V_{series}$ .<sup>15, 29</sup> As in Figure 2, Figure 4 shows higher dispersion of the results in CdS samples than for CdS/ZnS solar cells.

Comparing  $R_{rec}$  and  $C_\mu$  for passivated and reference cells it is possible to unravel the origin in the variation of  $V_{oc}$ .<sup>15, 29</sup> The higher  $V_{oc}$  observed after passivation, for some cases, can be due to: i) an upward shift of the conduction band (CB) of  $TiO_2$  and/or ii) a decrease of the recombination rate. Considering the first effect, an upward shift of the  $TiO_2$  CB, it produces a solidarity movement of the  $TiO_2$  electron quasi Fermi level, that determines the cell  $V_{oc}$ , and consequently an increase of open circuit potential. This displacement of the  $TiO_2$  CB can be identified by a shift to higher potentials of  $C_\mu$  (e.i. a horizontal shift of capacitance in Figure 4(b) and (d)). Moreover, the reduction of recombination rate can be also indentified with IS by an increase of  $R_{rec}$ . This recombination process corresponds to the recombination of electrons in  $TiO_2$ , which can either recombine with acceptor states in the electrolyte and/or in the semiconductor light absorber.<sup>16, 21</sup>

Taking into account these consideration some of the variations in the solar cell performance after passivation can be explained. For example, in the case of CdS QDSC passivated with DMA an upward shift of  $TiO_2$  CB is observed in Figure 4b. In addition, in Figure 4a shows a higher  $R_{rec}$  than the reference cell at higher  $V_F$  potentials. Both effects points in the direction of  $V_{oc}$  enhancement as it is in fact observed. Passivation with ETDA also shows a higher  $R_{rec}$  than the reference cell, but no significant shift of  $TiO_2$  CB, giving a lower enhancement in  $V_{oc}$  than in the case of DMA. Note also that the different behavior observed for the inorganic passivation THAC and TBAI for CdS and CdS/ZnS cells can be explained from the recombination resistances obtained after passivation. CdS electrodes passivated with  $Cl^-$  present higher  $R_{rec}$  and cell performance than CdS electrodes passivated with  $I^-$ , see Figure 4a. On the other hand the relative

values of  $R_{rec}$  for THAC and TBAI passivation are opposite for CdS/ZnS QDSCs and consequently the best performance is obtained for I<sup>-</sup> passivation in this case. Passivation reported here are surface treatments that can induce a shift in the TiO<sub>2</sub> CB and /or a change in the recombination properties of electrons in TiO<sub>2</sub>, the recombination process that can be scrutinized by IS, as it has been observed previously with molecular dipole treatments.<sup>24</sup>

Concerning the variation in photocurrent, the different electrodes show similar light absorbance, see SI2. This fact indicates that, in most of the cases, the changes observed in  $J_{sc}$  cannot be attributed to a variation in the light absorption properties after the passivation treatment. In these cases a reduction in recombination rate produces an increase of  $V_{oc}$ , as it has been already discussed, that also increase  $J_{sc}$  due to a shift of the J-V curve, and the reverse effect when recombination is augmented.



**Figure 4:** Recombination resistance,  $R_{rec}$ , extracted from the IS measurements in dark conditions for samples sensitized with (a) CdS and (c) CdS/ZnS; and chemical capacitance,  $C_{\mu}$ , for (a) CdS and (c) CdS/ZnS QDSCs. In order to calculate  $V_F$ , the applied DC voltage was corrected by subtracting the voltage drop due to the total series resistance.

Treatments with alkylamines (DMA and ETDA) and alkylthiols (EDT) enhances cell efficiency over the experimental error, see Figure 3d, even for CdS/ZnS cells. In spite of the contrasted goodness of ZnS coating to improve the efficiency of QDSCs,<sup>21-23</sup> it is not a perfect passivating agent, and it leaves more room for further QDSC performance improvement. On the other hand, the differences observed among alkylamines (DMA and ETDA) and alkylthiols (EDT) treated cells and additives bearing carboxylic groups (TGA and FA) that did not significantly improve or even worsen the performance of the cells, could be ascribed to the relatively low pKa of the carboxylic groups ( $pK_{a_{FA}}=3.77^{30}$  and  $pK_{a_{TGA}}=3.67^{31}$ ). This low pKa could induce the quantum dot corrosion or deactivation and its subsequent partial loss of functionality, see SI2.

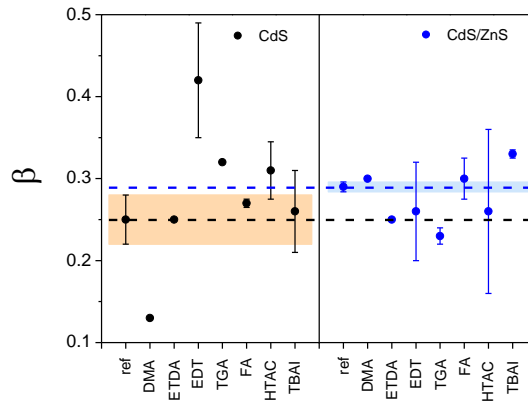
Moreover, it is well known that amines can enhance the luminescence of semiconductor particles by reducing the non-radiative recombination.<sup>26, 32</sup> An increase of luminescence was also observed for CdSe sensitized electrodes after ZnS coating.<sup>21</sup> Passivation of surface states reduces internal recombination in the QD (before injection, and non-accessible by IS experiments), enhancing the photoinjection and consequently the final photocurrent. In this sense, injection efficiency for QDSCs could be close to one, as it is considered for the most common dyes in DSCs,<sup>33</sup> only with an appropriate passivation .

Finally and concerning the evolution of cell parameters after passivation, a significant enhancement of FF is detected in most of the analyzed cases, see Figure 3c.

The increase of FF is especially significant for cells without ZnS coating, but even for CdS/ZnS electrodes further improvement can be attained after passivation. Variation of FF can be due to two reasons: i) a change in the series resistance or ii) a change in the  $\beta$  parameter, defined in Eq. (1).<sup>28, 29</sup> No significant change in the series resistance of passivated QDSCs was observed, as it has been analyzed by IS measurements of  $R_{series}$ , see SI3. Therefore, the increase of FF should be ascribed to an increase in  $\beta$  after passivation, as in fact is the general trend observed in Figure 5.  $\beta$  has been obtained from several samples and the average values plotted in Figure 5.  $\beta$  is calculated from the slope of Figure 4a and 4c graphs as:<sup>28, 29</sup>

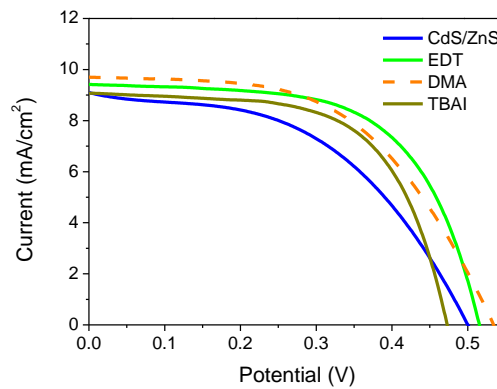
$$R_{rec} = R_0 \exp(-\beta q V_F / k_b T) \quad (1)$$

where  $R_0$  is a preexponential factor,  $q$ , the electron charge,  $k_b$  the Boltzmann constant and  $T$ , the temperature. Passivation produces a change in the recombination process that affects the  $\beta$  parameter, enhancing its value and consequently FF. The description of the exact physical mechanisms producing this change is below the scope of this work, and it will require a model for the  $\beta$  parameter in QDSCs that has not been developed yet.



**Figure 5:** Average value of  $\beta$  parameter, eq. (1), from the slope of  $\ln(R_{rec})$  vs.  $V_F$  (Figure 4a and 4c), obtained from CdS and CdS/ZnS reference QDSCs and for the cells with different passivations.

Once we observed that the best results were obtained with CdS/ZnS based devices and being conscious of the importance of the surface passivation on the efficiency of the cells, the chemical treatment was applied before and after coating the CdS with the ZnS layer, this means a double passivation treatment. In this case, only the treatments with an alkylamine, an alkylthiol and the inorganic iodine were tested. These treatments yielded the best performance of the devices with a single passivation, see Table 1. Figure 6 and Table 2 show the J-V curves and the cell parameters of the devices prepared with the double passivation methodology and in all cases the performance of the devices was improved compared to the reference device CdS/ZnS. Moreover, fill factor values were higher after the corresponding treatments, especially in the cases of EDT and TBAI with more than 20% enhancement, see Table 2, which is in agreement with the results previously obtained. It is worth to highlight that after the double treatment with EDT a record efficiency device ( $\eta \approx 3\%$ ) based on CdS/ZnS light absorber was obtained, which means a 105% enhancement of the efficiency compared to the reference device based on CdS (and a significant 33% enhancement respect the CdS/ZnS reference). This is as far as we now, one of the highest efficiency reported for QDSCs using only CdS as light absorbing material.

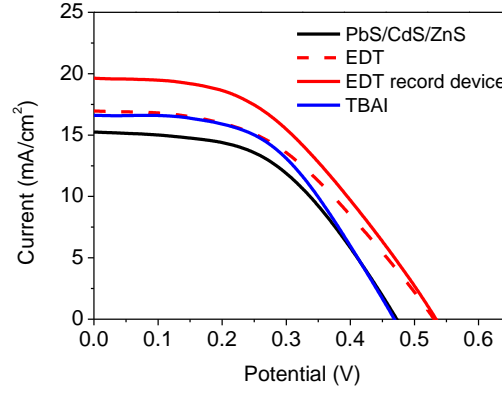


**Figure 6:** J-V curves of devices with double surface passivation based on CdS/ZnS light absorber.

**Table 2:** cell parameters for double surface passivation  
of CdS/ZnS based devices

	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
<b>CdS/ZnS</b>	0.500	9.08	49.6	2.23
<b>EDT</b>	0.515	9.60	60.1	2.97
<b>DMA</b>	0.534	9.78	52.9	2.76
<b>TBAI</b>	0.472	9.07	62.2	2.67

CdS is an excellent material for the analysis and optimization of different treatments and procedures for QDSCs due to its easy and relatively fast preparation by SILAR at room temperature and air atmosphere but the final efficiency is limited by its band gap that confines the visible light absorption to the shorter wavelengths, limiting consequently  $J_{sc}$ , see SI4. In contrast, PbS is a narrow band gap semiconductor that allows to extend the light absorption to the near infrared region,<sup>34-36</sup> see SI4. Taking advantage of the light absorbing properties of PbS nanocrystals and the use of our surface passivation methodology, we aimed for the development of high performance QDSC based on PbS/CdS/ZnS semiconductors. CdS/ZnS coating of PbS decreases recombination and enhances significantly the cell stability with polysulfide electrolyte.<sup>34</sup> Figure 7 and Table 3 show the averaged results and record cell obtained for PbS/CdS/ZnS based devices, where the double passivation treatment (after CdS and after ZnS deposition, no passivation was performed on PbS surface) was applied using EDT and TBAI. As in the previous analyzed cases, passivation treatments enhance the final solar cell performance, obtaining a record cell with  $\eta=4.67\%$ , 11% higher than our previous results with no passivation treatment (unpublished results). As far as we know this is the highest efficiency reported for a PbS based QDSCs. Note that in this case no significant enhancement of FF is observed due to the high increase of photocurrent that produces a higher voltage drop at the series resistance.



**Figure 7:** J/V curves of devices with double surface passivation based on PbS/CdS/ZnS as light absorber.

**Table 3:** cell parameters for the double surface passivation of PbS/CdS/ZnS based devices

	Voc (V)	Jsc (mA/cm <sup>2</sup> )	FF (%)	$\eta$ (%)
<b>PbS/CdS/ZnS</b>	0.471	15.37	49.8	3.57
<b>EDT<sup>a)</sup></b>	0.532	19.64	44.5	4.65
<b>EDT<sup>b)</sup></b>	0.529	16.98	45.6	4.09
<b>TBAI</b>	0.468	16.63	50.7	3.94

*a)* Record efficiency device values. *b)* Average values of different devices.

In summary, the effect of surface passivation in QDSCs with organic and inorganic compounds has been analyzed. In the case of organic passivation, alkylamines (DMA and ETDA) and alkylthiols (EDT) passivated cells improved the cell performance while carboxylic groups treatments (TGA and FA) did not contribute significantly or even worsen it. In the case of the inorganic passivation with I and Cl, it could also improve cell performance but in this case it is important on which material the treatment is performed, obtaining different results for I and Cl depending on the material (CdS or ZnS) in which the treatment is carried out. The origin of the observed differences in cell parameters has been explained by IS characterization. The increase of FF after passivation, due to an increase of the  $\beta$  parameter, is especially interesting. This observation is particularly remarkable for QDSCs, where low  $\beta$  are observed.<sup>15, 34, 37</sup> For



QDSCs the reported FF still not comparable with DSCs regardless of a significant reduction on the series resistance obtained with the use of alternative counter electrodes.<sup>15</sup> This work shows an efficient strategy to improve  $\beta$  value and consequently FF. This strategy has been used to improve conversion efficiency in CdS/ZnS and PbS/CdS/ZnS QDSCs, obtaining values as high as 2.97 and 4.65 % respectively, the highest reported for these systems up to our knowledge.

## **Associated Content**

**Supporting Information:** Materials and Methods, Light absorption measurements, Series resistance, IPCE for CdS, CdS/ZnS and PbS/CdS/ZnS.

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**Supporting Information Available:** Materials and methods, Light absorption measurements, Series resistance and IPCE for CdS, CdS/ZnS and PbS/CdS/ZnS. This material is available free of charge via the Internet <http://pubs.acs.org>.

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